at 105 °C. (The individual diene diastereomers could be isolated using a combination of columns B and E.) The isolated 2,4-heptadiene was identical in all respects with authentic material (Chemical Samples Co.) except in isomer distribution. By NMR spectral analysis and independent synthesis,[14] the product was found to be a mixture of *E,Z* and *Z,Z* diastereomers.

**6-Deuterio-2,4-heptadiene (10).** In a 250-mL three-neck round-bottom flask fitted with a dry ice condenser, dropping funnel and gas inlet tube was placed 70 mL of dry cyclohexane, 0.5 mL of freshly distilled quinoline, and 50 mg of Lindlar catalyst. Hydrogen gas was flushed through the flask held at 0 °C in an ice bath with vigorous stirring for several minutes before 1.00 g (10.5 mmol) of 6-deuterio-2-hepten-4-yne (**9**) was added. The reaction mixture was stirred under a positive pressure of hydrogen for 8 h as it was allowed to slowly warm from 0 to 25 °C. It was then filtered with the aid of Celite and preparatively separated from the solvent on GLC column C at 105 °C to give a mixture of *E,Z* and *Z,Z* diastereomers.[15] Electron impact mass spectrometric analysis showed the product to be 98% $d_1$ and 2% $d_0$.

**Acknowledgment** is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, to the Research Corporation under a Frederick Gardner Cottrell grant, and to Cleveland State University under a Faculty Research Initiation Award for the support of this research.

**Registry No.**—(*E*)-**3**, 2004-69-5; (*Z*)-**3**, 1574-40-9; (*E*)-**4**, 63640-74-4; (*Z*)-**4**, 63640-75-5; **5a**, 54354-36-8; **5b**, 31357-25-2; (*E*)-**6**, 63640-76-6; (*Z*)-**6**, 63640-77-7; (*E*)-**7**, 63640-78-8; (*Z*)-**7**, 63640-79-9; (*E*)-**8**, 63640-80-2; (*Z*)-**8**, 63640-81-3; (*E*)-**9**, 63640-82-4; (*Z*)-**9**, 63640-83-5; **10a**, 63640-84-6; **10b**, 63640-85-7; ethyl bromide, 74-96-4; propyl chloride, 540-54-5.

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(15) Lindlar reduction of enynes is well known to be stereospecific and cis: W. R. Roth and J. König, *Justus Liebigs Ann. Chem.*, **699**, 24 (1966); B. Wiedenmann and H. Hopf, *Z. Naturforsch. B*, **32**, 119 (1977).
(16) **Note Added in Proof.** Deuterium labeling experiments confirm that the diisobutylaluminum group does indeed add to C-4 of **4**.[14]

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# Synthesis of *exo*-(7-Bicyclo[4.1.0]heptyl)oxirane and *exo*-7-Vinylbicyclo[4.1.0]heptane

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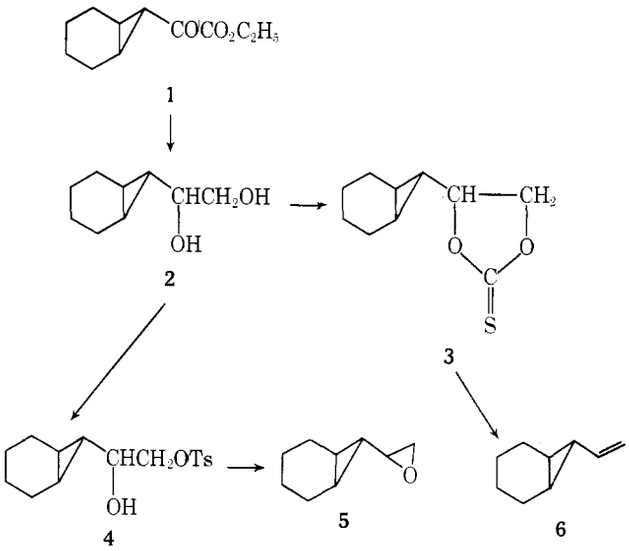
Although during the last few years many vinylcyclopropane and cyclopropyl oxirane derivatives have been prepared and their rearrangement investigated,[1] the relatively simple (7-bicyclo[4.1.0]heptyl)oxirane (**5**) still seems to be unknown and the synthesis of 7-vinylbicyclo[4.1.0]heptane (**6**) has been reported only recently.[2] In connection with another project, ethyl *exo*-(7-bicyclo[4.1.0]heptyl)glyoxylate (**1**) was synthesized in our laboratory.[3] This α-keto ester containing the bicyclo[4.1.0]heptyl moiety attached to a bifunctional two-carbon unit is a suitable starting material for the desired cyclopropane derivatives.

Reduction of the glyoxylate **1** with $LiAlH_4$ gave the diol **2**, a potential common precursor of both compounds **5** and **6**. According to the method of Corey and Winter,[4] the diol **2** was treated with thiocarbonyldiimidazole in refluxing toluene to convert it into the cyclic thionocarbonate **3**, which was converted to the desired olefin **6** by treatment with an excess of trimethyl phosphite at 110 °C.




The exo nature of the compounds all along the reaction sequence was proven by the oxidative conversion of both the diol **2** and the olefin **6** into the known *exo*-bicyclo[4.1.0]heptane-7-carboxylic acid.[5,10] In contrast with this result, in the direct vinylcyclopropanation of cyclohexene with vinyldiazomethane[2] a mixture of the exo and endo isomers was obtained, with the unusual preferential formation of the more congested endo isomer.

Epoxidation of the 7-vinylnorcarane **6** with *m*-chloroperbenzoic acid, a potential route to oxirane **5**, gave a complex product mixture. Systems having contiguous cyclopropane and epoxide rings are known to be rather unstable and the participation of the cyclopropane ring in developing neighboring carbocation centers is generally accepted to explain the formation of secondary products such as diols, esters, etc., instead of the desired aldehydes.[6] The synthesis of oxirane **5** has been accomplished in rather high yields by the selective tosylation of the diol **2**, followed by elimination of tosic acid from the monotosylate **4** under basic conditions.

## Experimental Section[7]

***exo*-(7-Bicyclo[4.1.0]heptyl)ethane-1,2-diol (2).**[8] To a magnetically stirred slurry of $LiAlH_4$ (6.0 g, 0.16 mol) in dry THF (100 mL) a solution of **1**[3] (3.2 g, 16 mmol) in THF (100 mL) was added dropwise at room temperature. After the addition was completed, the mixture was heated at reflux for 3.5 h, excess $LiAlH_4$ was destroyed by cautious addition of water (20 mL), followed by NaOH (10% solution, 10 mL), and the THF was removed. The residue was diluted with saturated NaCL solution and extracted with $CHCl_3$. On evaporation, the dried $CHCl_3$ extract gave 2.3 g (90%) of semisolid, crude diol **2**. The analytical sample, crystallized from hexane–pentane (3:2), melted at 52–54 °C: IR ($CHCl_3$) 3400 (br), 3500 $cm^{-1}$; NMR δ 0.35–1.0 (m, 3 H, cyclopropyl), 1.0–2.3 (m, 8 H, cyclohexane $CH_2$), 2.8–3.8 (m, 3 H, $-CHOHCH_2OH$); mass spectrum *m/e* 138($M^+ - H_2O$).

Anal. Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found: C, 69.50; H, 10.36.

**Monotosylation of Diol 2.** To an ice-cold solution of diol **2** (0.22 g, 1.46 mmol) in dry pyridine (7 mL) was added *p*-TsCl (0.3 g, 1.58 mmol). The mixture was kept in the refrigerator for 16 h, then 5% $NaHCO_3$ solution (15 mL) was added, followed by EtOAc (15 mL). The mixture was stirred for a few minutes, the phases were separated,

and the aqueous layer was extracted several times with $CHCl_3$. The combined organic layers were dried ($Na_2SO_4$), the solvent mixture was evaporated at reduced pressure (bath temperature 20–25 °C), and the last traces of pyridine were removed from the residue by repeated co-distillation with benzene. The residue (0.45 g) was purified by dry-column chromatography on silica gel (50 g). Elution was started with benzene (250 mL), followed by $CHCl_3$ to yield 0.37 g (85%) of the oily tosylate **4**, which was not further purified: IR ($CHCl_3$) 3600, 1360, 1170, 880 $cm^{-1}$; NMR $\delta$ 0.3–2.0 (m, 11 H, norcarane), 2.45 (s, 3 H, $-CH_3$), 3.0–3.3 (m, 1 H, –CHOH–), 3.8–4.25 (m, 2 H, $-CH_2OTs$), 7.3–7.9 (q, 4 H, aromatic); mass spectrum *m/e* 292 ($M^+ - H_2O$).

***exo*-(7-Bicyclo[4.1.0]heptyl)oxirane (5).** To the solution of crude tosylate **4** (8.1 g, 26 mmol) in dry glyme (150 mL) KOH pellets (3.5 g, 62.5 mmol) were added and the mixture was stirred magnetically at room temperature for 0.5 h, when TLC showed disappearance of the starting material. After filtration and evaporation of the solvent under reduced pressure, the residue was distilled to yield the oxirane **5** (3.1 g, 86%): bp 96–98 °C (20 mm); NMR $\delta$ 0.4–2.2 (m, 11 H, bicycloheptane ring protons), 2.3–2.8 (m, 3 H, epoxide ring protons); mass spectrum *m/e* 138.1049 ($M^+$ calcd for $C_9H_{14}O$: 138.10446).

***exo*-7-Vinylbicyclo[4.1.0]heptane (6).** A mixture of the diol **2** (1.87 g, 12 mmol) and *N,N'*-thiocarbonyldiimidazole[9] (2.03 g, 12 mmol) in dry toluene (25 mL) was heated at reflux for 1 h under $N_2$. The solvent was then removed, water (50 mL) was added, and the mixture was extracted with ether. The product, isolated from the ether solution, was purified by dry-column chromatography on silica gel. Elution with hexane–benzene (1:1) gave 1.43 g (52%) of oily thionocarbonate **3**: IR ($CHCl_3$) 1285 $cm^{-1}$; NMR $\delta$ 0.6–2.1 (m, 11 H, bicycloheptane ring protons), 4.2–4.8 (m, 3 H, five-membered ring protons); mass spectrum *m/e* 198 ($M^+$).

A mixture of the above thionocarbonate **3** (1.98 g, 10 mmol) and freshly distilled trimethyl phosphite (4 mL) was heated at reflux for 30 h under $N_2$. Excess of trimethyl phosphite was removed by distillation at 110–120 °C (760 mm), and the residue was distilled at 70–75 °C (28 mm) to yield 1.0 g (85%) of **6** contaminated with traces of trimethyl phosphite (NMR). An analytical sample was obtained by VPC (3% SE 30 on 100–120 mesh Chromosorb Q at 80 °C): IR ($CHCl_3$) 1630 $cm^{-1}$ (C=C); NMR $\delta$ 0.7–2.2 (m, 11 H, bicycloheptane ring protons), 4.6–5.1 (m, 2 H, $-H_AC{=}CH_BH_C$), 5.1–5.7 (m, 1 H, $H_A$) ($J_{AB}$ = 19, $J_{AC}$ = 12, $J_{BC}$ = 2 Hz); NMR spectrum was identical with that of an authentic sample of the exo isomer.[2]

Anal. Calcd for $C_9H_{14}$: C, 88.45; H, 11.55. Found: C,88.34; H, 11.47.

**Lead Tetraacetate Oxidation of Diol 2.** The diol **2** (0.39 g, 2.5 mmol) was oxidized with $Pb(OAc)_4$ (1.27 g, 2.8 mmol) in dry benzene (30 mL) at room temperature by the method described for the oxidation of *exo*-(7-bicyclo[4.1.0]heptyl)glycolic acid.[3] The resulting aldehyde was further oxidized with $Ag_2O$ to give the known *exo*-bicyclo[4.1.0]heptane-7-carboxylic acid (0.3 g, 85%): mp 97–98 °C (lit.[10] mp 97–99 °C); IR ($CHCl_3$) 1690 $cm^{-1}$; NMR $\delta$ 1.08–2.17 (m, 11 H); 12.1 (s, 1 H, –COOH); mass spectrum *m/e* 140 ($M^+$).

**Ozonation of Olefin 6.** Ozone was bubbled through an ice-cold magnetically stirred solution of olefin **6** (0.122 g, 1.0 mmol) in methylene chloride (20 mL). After the ozonation was completed (permanent blue color), the excess ozone was removed by passing nitrogen through the reaction mixture, and the solvent was removed under reduced pressure at low temperature.[11] To the residue acetone (A.R. Grade; 20 mL) was added and the magnetically stirred and cooled solution (ice bath) was titrated with Jones' reagent. After addition of water, the aqueous layer was extracted with methylene chloride (two 10-mL portions), and the combined organic layers were washed with saturated NaCl solution (20 mL), dried, and filtered. Evaporation of the solvent gave *exo*-bicyclo[4.1.0]heptane-7-carboxylic acid (0.13 g, 92%), identical with that obtained by the $Pb(OAc)_4$ oxidation of diol **2**.

**Acknowledgment.** We would like to thank Professor R. G. Salomon for providing the NMR spectra of *exo*- and *endo*-7-vinylbicyclo[4.1.0]heptanes for comparison.

**Registry No.**—**1**, 61558-26-7; **2**, 61558-30-3; **3**, 63076-63-1; **4**, 63076-64-2; **5**, 63076-65-3; **6**, 53951-19-2; *p*-TsCl, 98-59-9; *N,N'*-thiocarbonyldiimidazole, 6160-65-2; *exo*-bicyclo[4.1.0]heptane-7-carboxaldehyde, 4729-40-2; *exo*-bioyclo[4.1.0]heptane-7-carboxylic acid, 21448-77-1.

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(7) Melting points were taken in capillaries and are uncorrected. The IR spectra were determined on a Perkin-Elmer infrared spectrophotometer. NMR were recorded on a Varian T-60 or on a Varian A-60 spectrometer in $CDCl_3$ solution using $Me_4Si$ as internal standard.
(8) The formation of this diol as a by-product in the $NaBH_4$ reduction of **1** was observed and described by us recently.[3]
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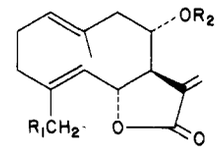
(11) Caution! Since ozonides are potentially dangerous, this operation should be carried out behind a safety shield.

# Communications

## An Approach to the Synthesis of Complex Germacranes. A New Route to Highly Functionalized 9-Methyl-1-decalones

*Summary:* Reductive C-methylation of $\alpha$-tetralones in liquid ammonia provides a general, high-yielding procedure for the synthesis of 9-methyl-1-decalones suitable for the synthesis of germacranes and related sesquiterpenes.

*Sir:* Several ingenious approaches to the synthesis of the simpler germacranes have been reported.[1] The preparation of more complex representatives, e.g., tulipinolide (**1**)[2] and cnicin (**2**),[3] whose cytoxic properties have aroused considerable interest,[4] poses problems of a much greater magnitude.




**1** $R_1$=H, $R_2$=$COCH_3$

**2** $R_1$=OH, $R_2$=$COC(CH_2)CH(OH)CH_2OH$

While the fragmentation of a suitable decalin derivative (Scheme I) with the oxygenation pattern indicated (*) in structure **3**[5] appeared to offer a possible method, this pattern of functionality does not arise readily from traditional decalin syntheses.[1,6] A novel approach was indicated. We report that the reductive alkylation of $\alpha$-tetralone derivatives[7] offers a flexible and efficient entry to the synthesis of such decalins.